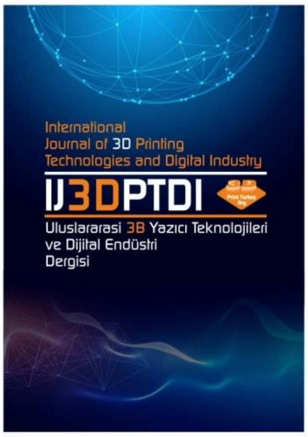


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# POLYACRYLONITRILE (PAN) ELECTROSPUN NANOFIBERS COATED 3D PRINTED PLA MATERIALS WITH DIFFERENT INFILL PATTERNS AND THEIR TENSILE PROPERTIES

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## ABSTRACT

In this study, the mechanical properties of 3D printed polylactic acid (PLA) samples produced with fused deposition modeling (FDM) technology with five different infill patterns; trihexagon, triangle, line, gyroid, and grid, and these patterns were compared for their mechanical properties. In the second part of the study, PLA specimens with different infill patterns were covered with polyacrylonitrile (PAN) nanofibers synthesized by the electrospinning method to enhance their PLA poor mechanical properties. In the tensile tests, among the infill patterns, gyroid showed the highest Young Modulus with 1108 MPa. SEM results showed that PAN electrospun nanofibers were beadless and ordered nanofibers with an average diameter of 165.7±33 nm. The results showed that after PAN nanofibers coating on PLA specimens, the mechanical properties of the samples for all infill patterns improved, and tensile strain values and therefore, ductile behaviour of all specimens increased. PAN nanofibers could significantly enhance the stiffness of 3D printed PLA materials.

**Keywords:** 3D printing, PLA, Infill Pattern, Electrospinning, PAN, Mechanical Properties.

## 1. INTRODUCTION

Three-Dimensional (3D) Printing is a production method of creating 3D objects by printing material layer by layer, that is, by melting and solidifying it [1]. The 3D printing system consists of a print bed, extruder with a hot-end nozzle, stepper motors, filament feed tube, and a microcontroller such as Arduino that uses open-source software [2], and controls the movement of the extruder through stepper motors in 3 dimensions.

Fused deposition modeling (FDM) is a widely utilized additive manufacturing method to produce high-quality products with complex geometries at a low cost, quality and efficiency. Besides, this 3D printing technology allows the development of products with different mechanical properties by testing different FDM parameters [3].

Thermoplastic polymers such as acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) are the most commonly utilized in non-metallic 3D printing [4]. PLA is often found used in 3D printing due to its availability, lightweight, and biocompatibility. Although the mechanical properties of 3D printed PLA are better compared to ABS [5], PLA is a brittle material [6] and studies to improve the mechanical properties of 3D printed PLA continue. Different methods were tried for this purpose. Some different reinforcement materials such as copper [7] and carbon nanotubes [8] were investigated to enhance the mechanical properties of PLA in the literature. Hybridization with a different method with 3D printing is another way utilized to improve the mechanical properties of 3D printed PLA.

The electrospinning technique provides a convenient approach to producing continuous nano-scale fibers [9]. Electrospun nanofibers are important nanomaterials with their large high porosity, specific surface area, small pore size, and well-connected pore structure [10] and find use in many application areas; filtration membranes [11], drug delivery [12], tissue engineering [13, 14], catalysts [15], actuators [16], food packaging [17], etc.

Polyacrylonitrile (PAN) which is a synthetic polymer having a semi-crystalline structure, is thermally stable and degrades over 300 °C [18]. PAN electrospun nanofibers are widely utilized for different applications due to their unique thermal stability, superior mechanical properties, and good solvent resistance [19].

In literature, studies in which 3D printing and electrospinning methods are used together are very limited. These two methods have been utilized together for rapid response hydrogel actuators [20], tissue engineering [21, 22, 23], filter materials [24], and textile applications [25]. In this study, by using 3D printing and electrospinning technologies together, it was aimed to enhance the poor mechanical properties and the stiffness of 3D printed PLA specimens with different infill patterns.

## 2. MATERIALS AND METHOD

### 2.1 Materials

PLA in the form of filament with a diameter of 1.75 mm was purchased from Porima. PAN (MW=150.000, CAS No: 25014-41-9), and N,N-dimethylformamide (DMF, anhydrous, 99.8%, CAS No.: 68-12-2) were purchased from Sigma-Aldrich to produce PAN electrospun nanofibers.

### 2.2. 3D Printing Process of PLA Samples

Five infill patterns, trihexagon, triangle, line, gyroid, and grid were chosen to compare their mechanical properties and they were produced in dog-bone shape to determine basic mechanical properties by the FDM method. The height of dog-bone shaped specimens is 80 mm, the width is 10mm, and the thickness is 4mm.

The specimens were printed using a Pidu Z100 3D Printer. The material, 1.75 mm PLA filament, and the specimen printing temperature was set at 210°C for the printing process. The software utilized for controlling the printing parameters was Ultimaker Cura. Figure 1 shows the 3D printer utilized in this study and the PLA dog bone specimens printed at different infill patterns.

Mechanical tests of PLA specimens were carried out with a constant cross-head speed of 5 mm/min by an Instron 3366 universal testing machine according to the ASTM D 638-14 [26].

### 2.3. Electrospinning of PAN Nanofibers

In order to prepare the PAN electrospinning solution, 0.41 g PAN was dissolved in 5ml DMF (8 wt%) with a mechanical stirrer at 60 °C. Then the prepared solution was loaded into a 5 ml syringe and connected to the high voltage power supply. The electrospinning parameters were optimized for PAN solution. The applied voltage was set as 15 kV and the flow rate of the solution was set to 1.5 μl/h. The working distance was 30 cm for beadless and regular fiber growth. The obtained PAN nanofibers were deposited on a plate collector. The collector is a square shape plate and covered with Al foil. The electrospinning process lasted for 1 h and after spinning process, the PAN nanofibrous film was peeled off from the Al foil and adhered to the PLA samples with a very thin layer of adhesive. All 3D-printed dog-bone shaped PLA samples were coated identically with the PAN nanofibers. The morphology and the diameter of the PAN nanofibers were investigated by scanning electron microscopes (SEM) with an accelerating voltage of 5 kV.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Tensile Test Results of the 3D Printed PLA Samples

Tensile tests of 3D printed specimens with the infill pattern of trihexagon, triangle, line, gyroid, and grid were performed and the load-displacement curves during tensile tests of the 3D printed PLA samples with various infill patterns were displayed in Fig. 2. The results indicated that infill patterns had a significant influence on tensile properties. The max tensile strain values were exhibited for gyroid and line infill patterns with 5.39 and 5.26%, respectively, while trihexagone showed the lowest tensile strain values of 2.94% (Table 1). Therefore, the gayroid was found as the most ductile infill pattern. When the Young's Modulus of the PLA specimens were examined, it was indicated that the gyroid and trihexagon showed the highest values of Young's Modulus with 1108 and 1110 MPa, respectively. Young's Modulus of Triangle was 1033 MPa and the lowest value was observed for line pattern (Fig. 3). It can be inferred from the results that gyroid as an infill pattern was favored among the five examined patterns in terms of mechanical properties. This result is in agreement with the results of relevant studies in the literature that showed gyroid good mechanical properties [27, 28]. It was probably due to the low anisotropy of the gyroid structure [29].

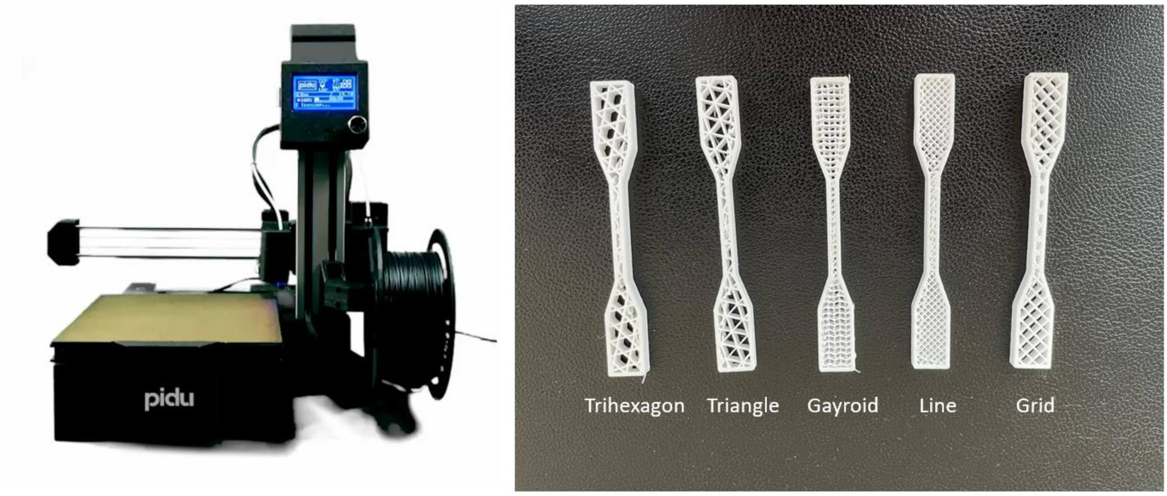


**Figure 1**.3D printer utilized in this study and the dog-bone shaped PLA specimens at different infill patterns printed with this printer.

**Table 1** Sample codes, infill patterns and their tensile properties.

| Sample Code | Infill | Young's Modulus (MPa) | Tensile strain at Break (%) |
|---|---|---|---|
| PLA1 | Trihexagone | 1110 | 2.94 |
| PLA2 | Triangle | 1033 | 4.05 |
| PLA3 | Line | 882 | 5.26 |
| PLA4 | Gyroid | 1108 | 5.39 |
| PLA5 | Grid | 911 | 4.38 |
| PLAPAN1 | Trihexagone | 1042 | 4.51 |
| PLAPAN2 | Triangle | 921 | 5.48 |
| PLAPAN3 | Line | 823 | 6.45 |
| PLAPAN4 | Gyroid | 901 | 6.68 |
| PLAPAN5 | Grid | 830. | 4.51 |

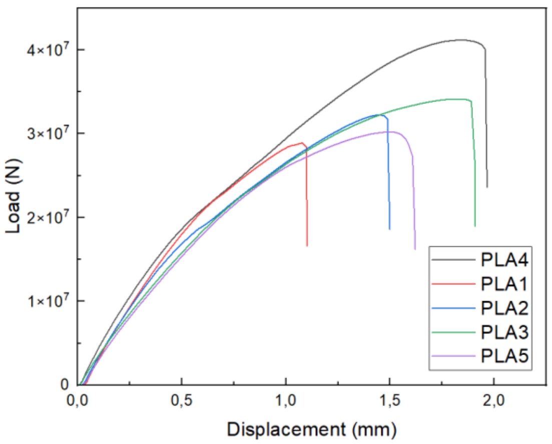


**Figure 2.** Load-displacement curves of the 3D printed PLA samples with different infill patterns.

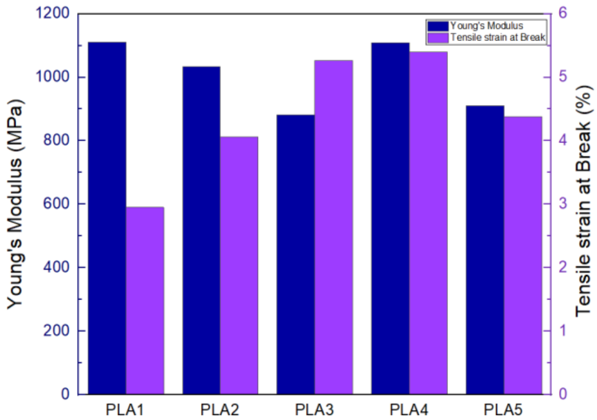


**Figure 3.** Tensile properties of the 3D printed PLA samples with different infill patterns.

### 3.2. Characterization of PAN Electrospun Nanofibers

Fig.4a shows the SEM image of electrospun PAN nanofibers obtained by the electrospinning method at 25000X magnification. Obtained PAN nanofibers which showed cylindrical shape, were regular and beadless.

The average fiber diameter was measured as 165.7±33 nm from the SEM image and the diameter distribution of the nanofibrous sample was given in Fig. 4b. It was observed that the diameter of the nanofibers is mostly in the range of 140-200 nm.

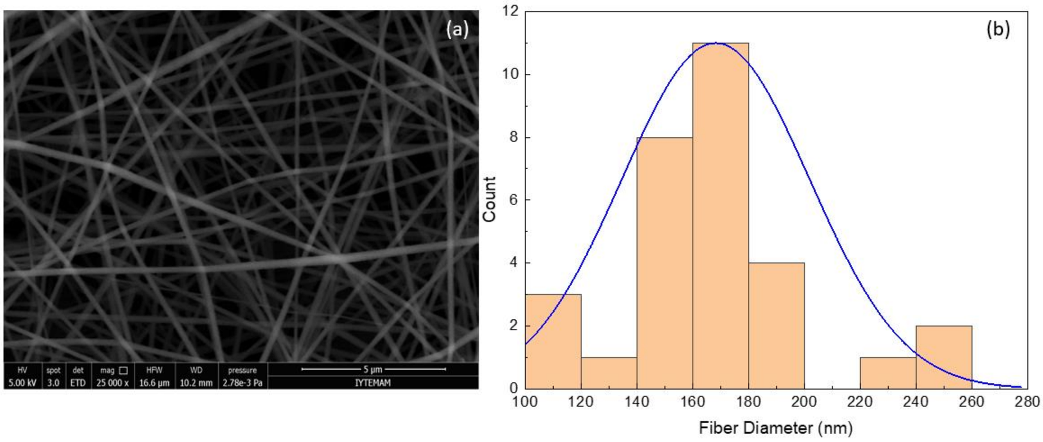


**Figure 4**. (a) SEM image of PAN electrospun nanofibers at 25000X magnification (b) Diameter distribution of PAN nanofibers.

### 3.3. Mechanical Characterization of PAN nanofibers coated-3D printed PLA samples with different infill patterns

PLA is an economical, safe, environmentally friendly, high strength, high modulus, and biocompatible thermoplastic polymer, besides it is easily processable [30, 31]. However, PLA is a very brittle material with less than 10% elongation at break [29]. In this study, to enhance the mechanical properties of PLA, PAN nanofibers were utilized. Tensile tests of PAN electrospun nanofiber coated 3D printed PLA specimens with the infill pattern of trihexagon, triangle, line, gyroid, and grid were carried out and the load-displacement curves and tensile properties were given in Fig. 5 and Fig. 6, respectively. The results indicated that after coating with PAN nanofibers, for all infill patterns Young's modulus of the PLA specimens decreased while tensile strain values of the specimens increased. Especially, for trihexagone, the increase in the tensile strain after nanofiber coating was about 2-fold compared to neat PLA specimen. The max tensile strain value was observed again for gyroid with 6.686%, while trihexagone and grid showed the lowest tensile strain values of 4.51% (Table 1).

Overall, the mechanical test results proved that PAN electrospun nanofibers enhanced the stiffness of the PLA specimens for all infill patterns. Besides, the gyroid infill pattern was favored among the five examined patterns in terms of mechanical properties for both neat PLA and PAN nanofiber-coated PLA specimens.

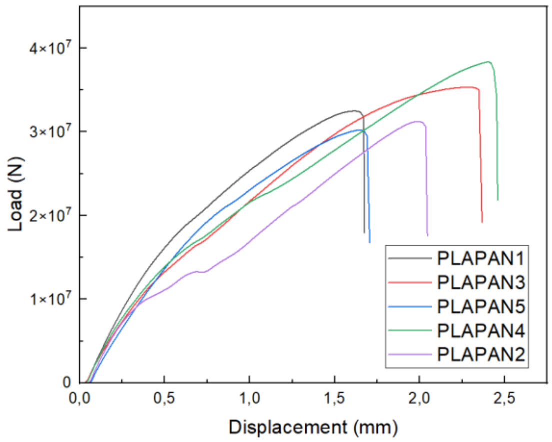


**Figure 5** Load-displacement curves of the PAN nanofibers coated-3D printed PLA samples with different infill patterns.

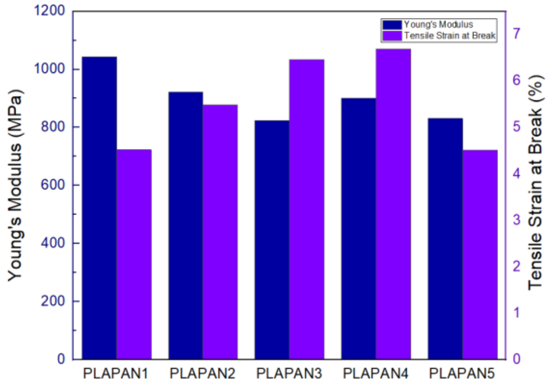


**Figure 6** Tensile properties of the PAN nanofibers coated-3D printed PLA samples with different infill patterns.

## 4. CONCLUSIONS

In this study, the tensile properties of 3D printed PLA specimens with five different infill patterns were investigated. The infill patterns influenced significantly the tensile properties of the material. In general, the results showed that the gyroid infill pattern provided both high Young's modulus and high tensile strain. Moreover, to improve the stiffness of 3D printed PLA specimens, PAN nanofibers were produced by the electrospinning method and covered on the PLA specimens. PAN electrospun nanofibers improved the stiffness of PLA specimens for all infill patterns by increasing their tensile strain values. The gyroid pattern demonstrated good mechanical properties before and after coating, however, after PAN nanofiber coating, the tensile strain and therefore, ductile behaviour of the trihexagon infill pattern which showed the highest Young's Modulus, were also enhanced. The resulting hybrid material is a very suitable material to use in air and water filters, especially with its porous surface and ductile structure.

## CONFLICT OF INTEREST

The author declares that there is no conflict of interest.

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